Polymers, 2018, vol.10, N8

Influence of the cross-link density on the rate of crystallization of poly(ε-caprolactone)

Sedov I., Magsumov T., Abdullin A., Yarko E., Mukhametzyanov T., Klimovitsky A., Schick C.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2018 by the authors. Cross-linked poly(ε-caprolactone) (PCL) is a smart biocompatible polymer exhibiting two-way shape memory effect. PCL samples with different cross-link density were synthesized by heating the polymer with various amounts of radical initiator benzoyl peroxide (BPO). Non-isothermal crystallization kinetics was characterized by means of conventional differential scanning calorimetry (DSC) and fast scanning calorimetry (FSC). The latter technique was used to obtain the dependence of the degree of crystallinity on the preceding cooling rate by following the enthalpies of melting for each sample. It is shown that the cooling rate required to keep the cooled sample amorphous decreases with increasing cross-link density, i.e., crystallization process slows down monotonically. Covalent bonds between polymer chains impede the crystallization process. Consequently, FSC can be used as a rather quick and low sample consuming method to estimate the degree of cross-linking of PCL samples.

http://dx.doi.org/10.3390/polym10080902

Keywords

Cross-linking, Crystallization kinetics, Differential scanning calorimetry, Fast scanning calorimetry, poly(ε-caprolactone)

References

[1] Global Polycaprolactone Market to Reach US$ 214.2 Mn by an End of 2021, Persistence Market Research (PMR) Report 2016. Available online: https://www.persistencemarketresearch.com/mediarelease/ polycaprolactone-market.asp (accessed on 1 August 2018)

[2] Jenkins, M. (Ed.) Biomedical Polymers; Woodhead Publishing in Materials; Woodhead Publ.: Cambridge, UK, 2007; ISBN 978-1-84569-070-0

[3] Merkli, A.; Tabatabay, C.; Gurny, R.; Heller, J. Biodegradable polymers for the controlled release of ocular drugs. Prog. Polym. Sci. 1998, 23, 563-580

[4] Sinha, V.R.; Bansal, K.; Kaushik, R.; Kumria, R.; Trehan, A. Poly-∈-caprolactone microspheres and nanospheres: An overview. Int. J. Pharm. 2004, 278, 1-23

[5] Vieira, A.C.; Vieira, J.C.; Guedes, R.M.; Marques, A.T. Degradation and Viscoelastic Properties of PLA-PCL, PGA-PCL, PDO and PGA Fibres. Mater. Sci. Forum 2010, 636-637, 825-832

[6] Yang, L.; Li, J.; Jin, Y.; Li, M.; Gu, Z. In vitro enzymatic degradation of the cross-linked poly('-caprolactone) implants. Polym. Degrad. STable 2015, 112, 10-19

[7] Pandini, S.; Passera, S.; Messori, M.; Paderni, K.; Toselli, M.; Gianoncelli, A.; Bontempi, E.; Riccò, T. Two-way reversible shape memory behaviour of crosslinked poly('-caprolactone). Polymer 2012, 53, 1915-1924

[8] Pitt, C.G.; Chasalow, F.I.; Hibionada, Y.M.; Klimas, D.M.; Schindler, A. Aliphatic polyesters. I. The degradation of poly(∈-caprolactone) in vivo. J. Appl. Polym. Sci. 1981, 26, 3779-3787

[9] Jenkins, M.J.; Harrison, K.L. The effect of crystalline morphology on the degradation of polycaprolactone in a solution of phosphate buffer and lipase. Polym. Adv. Technol. 2008, 19, 1901-1906

[10] Wang, Z.; Jiang, B. Crystallization Kinetics in Mixtures of Poly('-caprolactone) and Poly(styrene-coacrylonitrile). Macromolecules 1997, 30, 6223-6229

[11] L'Abee, R.; Van Duin, M.; Goossens, H. Crystallization kinetics and crystalline morphology of poly('-caprolactone) in blends with grafted rubber particles. J. Polym. Sci. Part B Polym. Phys. 2010, 48, 1438-1448

[12] Madbouly, S.A. Isothermal crystallization kinetics in binary miscible blend of poly('-caprolactone)/tetramethyl polycarbonate. J. Appl. Polym. Sci. 2007, 103, 3307-3315

[13] Madbouly, S.A. Nonisothermal Crystallization Kinetics of Miscible Blends of Polycaprolactone and Crosslinked Carboxylated Polyester Resin. J. Macromol. Sci. Part B 2011, 50, 427-443

[14] Lai, S.L.; Ramanath, G.; Allen, L.H.; Infante, P.; Ma, Z. High-speed (104 °C/s) scanning microcalorimetry with monolayer sensitivity (J/m 2). Appl. Phys. Lett. 1995, 67, 1229-1231

[15] Schick, C.; Mathot, V. (Eds.) Fast Scanning Calorimetry; Springer International Publishing: Cham, Switzerland, 2016; ISBN 978-3-319-31327-6, 978-3-319-31329-0

[16] Schick, C.; Androsch, R. Fast Scanning Chip Calorimetry. In Handbook of Thermal Analysis and Calorimetry; Elsevier: New York, NY, USA, 2018; Volume 6, pp. 47-102. ISBN 9780444640628

[17] McCluskey, P.J.; Vlassak, J.J. Parallel nano-Differential Scanning Calorimetry: A New Device for Combinatorial Analysis of Complex nano-Scale Material Systems. MRS Proc. 2006, 924

[18] Lopeandía, A.F.; Cerdó, L. l.; Clavaguera-Mora, M.T.; Arana, L.R.; Jensen, K.F.; Muñoz, F.J.; Rodríguez-Viejo, J. Sensitive power compensated scanning calorimeter for analysis of phase transformations in small samples. Rev. Sci. Instrum. 2005, 76, 065104

[19] Mathot, V.; Pyda, M.; Pijpers, T.; Vanden Poel, G.; van de Kerkhof, E.; van Herwaarden, S.; van Herwaarden, F.; Leenaers, A. The Flash DSC 1, a power compensation twin-type, chip-based fast scanning calorimeter (FSC): First findings on polymers. Thermochim. Acta 2011, 522, 36-45

[20] Minakov, A.A.; Schick, C. Ultrafast thermal processing and nanocalorimetry at heating and cooling rates up to 1MK/s. Rev. Sci. Instrum. 2007, 78, 073902

[21] Denlinger, D.W.; Abarra, E.N.; Allen, K.; Rooney, P.W.; Messer, M.T.; Watson, S.K.; Hellman, F. Thin film microcalorimeter for heat capacity measurements from 1.5 to 800 K. Rev. Sci. Instrum. 1994, 65, 946-959

[22] Androsch, R.; Schick, C. Interplay between the Relaxation of the Glass of Random L/D-Lactide Copolymers and Homogeneous Crystal Nucleation: Evidence for Segregation of Chain Defects. J. Phys. Chem. B 2016, 120, 4522-4528

[23] Schawe, J.E.K. Cooling rate dependence of the crystallinity at nonisothermal crystallization of polymers: A phenomenological model. J. Appl. Polym. Sci. 2016, 133

[24] Toda, A.; Androsch, R.; Schick, C. Insights into polymer crystallization and melting from fast scanning chip calorimetry. Polymer 2016, 91, 239-263

[25] Zhuravlev, E.; Madhavi, V.; Lustiger, A.; Androsch, R.; Schick, C. Crystallization of Polyethylene at Large Undercooling. ACS Macro Lett. 2016, 5, 365-370

[26] Wurm, A.; Zhuravlev, E.; Eckstein, K.; Jehnichen, D.; Pospiech, D.; Androsch, R.;Wunderlich, B.; Schick, C. Crystallization and Homogeneous Nucleation Kinetics of Poly('-caprolactone) (PCL) with Different Molar Masses. Macromolecules 2012, 45, 3816-3828

[27] Zhuravlev, E.; Schmelzer, J.W.P.; Wunderlich, B.; Schick, C. Kinetics of nucleation and crystallization in poly('-caprolactone) (PCL). Polymer 2011, 52, 1983-1997

[28] Zhuravlev, E.; Wurm, A.; Pötschke, P.; Androsch, R.; Schmelzer, J.W.P.; Schick, C. Kinetics of nucleation and crystallization of poly('-caprolactone)-Multiwalled carbon nanotube composites. Eur. Polym. J. 2014, 52, 1-11

[29] Hirschl, C.; Biebl-Rydlo, M.; DeBiasio, M.; Mühleisen, W.; Neumaier, L.; Scherf, W.; Oreski, G.; Eder, G.; Chernev, B.; Schwab, W.; et al. Determining the degree of crosslinking of ethylene vinyl acetate photovoltaic module encapsulants-A comparative study. Sol. Energy Mater. Sol. Cells 2013, 116, 203-218

[30] Flory, P.J.; Rehner, J. Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. J. Chem. Phys. 1943, 11, 521-526

[31] Bordes, C.; Fréville, V.; Ruffin, E.; Marote, P.; Gauvrit, J.Y.; Briançon, S.; Lantéri, P. Determination of poly('-caprolactone) solubility parameters: Application to solvent substitution in a microencapsulation process. Int. J. Pharm. 2010, 383, 236-243

[32] Barton, A.F.M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters, 2nd ed.; CRC Press: Boca Raton, FL, USA, 1991; ISBN 978-0-8493-0176-6

[33] Wurm, A.; Merzlyakov, M.; Schick, C. Reversible Melting During Crystallization of Polymers Studied by Temperature Modulated Techniques (TMDSC, TMDMA). J. Therm. Anal. Calorim. 2000, 60, 807-820

[34] Skoglund, P. Fransson, ke Continuous cooling and isothermal crystallization of polycaprolactone. J. Appl. Polym. Sci. 1996, 61, 2455-2465

[35] Jeziorny, A. Parameters characterizing the kinetics of the non-isothermal crystallization of poly(ethylene terephthalate) determined by d.s.c. Polymer 1978, 19, 1142-1144

[36] Gaylord, R.J. A theory of the stress-induced crystallization of crosslinked polymeric networks. J. Polym. Sci. Polym. Phys. Ed. 1976, 14, 1827-1837

[37] Tosaka, M.; Senoo, K.; Kohjiya, S.; Ikeda, Y. Crystallization of stretched network chains in cross-linked natural rubber. J. Appl. Phys. 2007, 101, 084909

[38] Jiao, C.;Wang, Z.; Liang, X.; Hu, Y. Non-isothermal crystallization kinetics of silane crosslinked polyethylene. Polym. Test. 2005, 24, 71-80

[39] Mandelkern, L. Crystallization of Polymers, 2nd ed.; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2002; ISBN 978-0-521-81681-6

[40] Brown, P.S.; John, M.; Loadman, R.; Tinker, A.J. Applications of FT-NMR to Crosslink Density Determinations in Natural Rubber Blend Vulcanizates. Rubber Chem. Technol. 1992, 65, 744-760

[41] Bin Ahmad, A.; Bin Amu, A. Estimation of crosslink density by solid-state NMR spectroscopy. In Blends of Natural Rubber; Tinker, A.J., Jones, K.P., Eds.; Springer Netherlands: Dordrecht, The Netherlands, 1998; pp. 40-52. ISBN 978-94-010-6064-6

[42] Radusch, H.-J.; Kolesov, I.; Gohs, U.; Heinrich, G. Multiple Shape-Memory Behavior of Polyethylene/Polycyclooctene Blends Cross-Linked by Electron Irradiation. Macromol. Mater. Eng. 2012, 297, 1225-1234